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An overview of hydrogen gas production from solar energy

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A B S T R A C T

Hydrogen production plays a very important role in the development of hydrogen economy.

Hydrogen gas production through solar energy which is abundant, clean and renewable is one of the promising hydrogen production approaches. This article overviews the available technologies for hydrogen generation using solar energy as main source.

Photochemical, electrochemical and thermochemical processes for producing hydrogen with solar energy are analyzed from a technological environmental and economical point of view. It is concluded that developments of improved processes for hydrogen production via solar resource are likely to continue in order to reach competitive hydrogen production costs. Hybrid thermochemical processes where hydrocarbons are exclusively used as chemical reactants for the production of syngas and the concentrated solar radiation is used as a heat source represent one of the most promising alternatives: they combine conventional and renewable energy representing a proper transition towards a solar hydrogen economy.

Contents

1. Introduction

The critical energy situation of the world raises serious concerns and projects on the horizon, energy and environmental crisis. The growing energy demand coupled with the depletion of fossil resources, the accentuation of climate change, the fragility and dangers of nuclear power recently witnessed at Chernobyl and Fukushima, raised an obvious question; what alternative is there in our society to come out of this energy slump?

After the era of fossil fuel, renewable energy (notably solar) appears as a strong driving force capable of maintaining the availability of energy with hydrogen as energy carrier. Hydrogen with its properties listed in Table 1 is presented as one of the

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Table 1
Physico-chemical characteristics hydrogen [1].

Properties	Numerical values
ICP (inferior calorific power)	10,800 kJ/Nm^3 or 33.33 kWh/kg
SCP (superior calorific power)	12,770 kJ/Nm^3 or 39.41 kWh/kg
Gaseous density 20.3 K and 273 K	1.34 kg/m^3/0.08988 kg/m^3
Liquid density 20.3 K	70.79 kg/m^3
Specific heat capacities *Cp*/*Cv*	14,266/10,300 J/kg K
Heat capacity of vaporization	445.4 kJ/kg

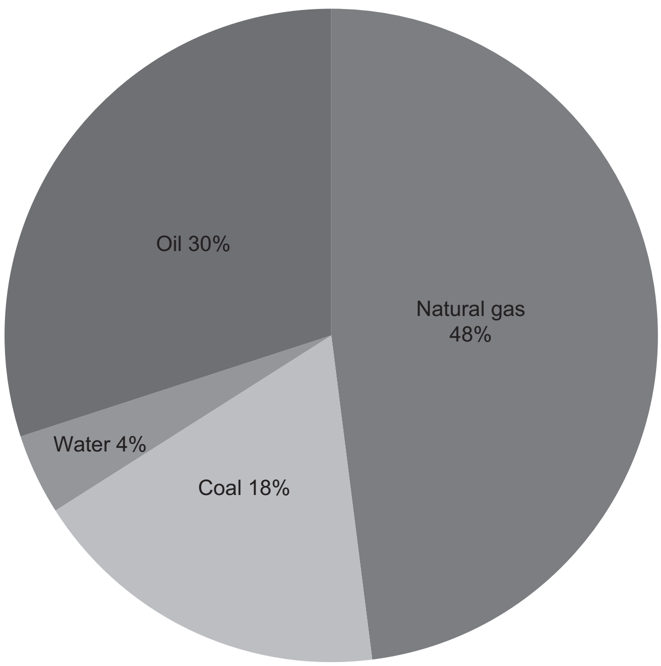


Fig. 1. Distribution of the modes of hydrogen production [2].

alternative energy carrier [1]. What is it really? Is hydrogen the actual solution to all future energy provision problems?

In order to answer the existing question about hydrogen as an alternative energy carrier and hydrogen as a future energy survival, many different techniques have been exploited. Currently hydrogen production through advanced technologies using fossils [2] (Fig. 1) is realized at 95% in particular by steam reforming of natural gas (48%) [3]. Hydrogen production from other fossil resources (Hydrocarbon 30% and Coal 18%) is principally obtained by the process of partial oxidation. The last advanced process of hydrogen production is by the electrolysis of pure alkaline water as a function of the raw material which permits an answer to 4% of the world's demand [2,3]. This recourse of fossil resources which is not only a raw material for hydrogen but also an energy source for the processes posed two major problems namely: the depletion of resources and the increase of the concentrations of carbon dioxide and Methane; main greenhouse gases in the atmosphere, as they contributes respectively 63% and 19% of the peak [4]. As an illustration, the average of only carbon dioxide emitted to the atmosphere with respect to the amount of methane gas being consumed as analyzed by the process of steam reforming stands at 9 kg/kg of hydrogen [5].

The scarcity of fossil resources and the consequent emission of CO_2 and CH_4 into the environment drive us to revise means for this energy mixed up in order to satisfy both the needs of the local population and the industries.

Renewables are an emissions-free way to produce hydrogen, and, conversely, hydrogen offers a way for renewables to generate transportation fuel and reliable power. The versatility of renewable technologies allows them to be adapted to meet diverse energy needs. Though costs for some renewable technologies are higher than traditional generated sources, technological advancements and increased in demand in the energy market has lead to reduction prices. Additionally, the environmental benefits help to compensate for the higher costs. When taken as a whole, the future conjunction of hydrogen and renewable energy technology is a promising one.

Solar energy is potentially the most abundant renewable energy resource available to us and hydrogen production from solar energy is considered to be the ultimate solution for sustainable energy. Many researchers have been involved in analyzing the different solar hydrogen production methods based on energy and exergy analysis. Wang et al. [6] have examined the solar-to-hydrogen reaction mechanisms including thermochemical cycles that utilize heat to split water molecules, electrolysis that utilizes electric potential to split water molecules, and photochemical processes that utilize photon-activated electrons of auxiliary reagents (sensitizer and catalyst) to activate and split water molecules. An overview of theory and current technological status of hydrogen from Solar Energy was done by Erickson and Goswami [7]. The Exergetic assessment of solar hydrogen production methods was investigated by Joshi et al. [8]. They have classified the solar hydrogen production system based on the energy input and solar thermal, type of chemical reactants and for different hydrogen production processes involved for example, electrolysis, reforming, gasification, cracking etc. For a case study they have analyzed the sustainability of a solar PV based hydrogen system through exergy efficiency and sustainability index. Later Joshi et al. [9] have made the comparison of sustainability index for solar thermal and photovoltaic (PV) hydrogen production systems.

Among the many techniques of solar hydrogen production identified, some have reached a stage of industrial and commercial maturity, and others are the subject of research. These technologies beyond their diversity are grouped into three families: photochemical, thermochemical and electrochemical technologies that offer a promising alternative for the storage of solar energy.

The objective of this work is to make a large inventory of fixtures of these technologies of hydrogen production through solar energy which brings out the necessary elements responding to a number of questions and even the problems earlier mentioned. The methodology of the study made below is at first technological. The environmental and economical stakes relative to an economic development of hydrogen through solar means will be approached. This will ensure some degree of reflection on the viability and future perspectives on the production and use of solar hydrogen as an energy vector especially for regions endowed with sufficient solar radiation.

2. Hydrogen production from new energy

The recourse on exhaustible fossils sources for hydrogen production contributes greatly to the increase in the greenhouse effect. This is what would have been taken care of technically and financially (harnessing CO_2 or ecotax), capable of modifying the thresholds of alternative competitive economic solutions particularly renewable energy [10]. The development of the methods of hydrogen production based on renewable energy sources takes place as much as possible without releasing the greenhouse gas [11]. These methods represent alternative ways for hydrogen

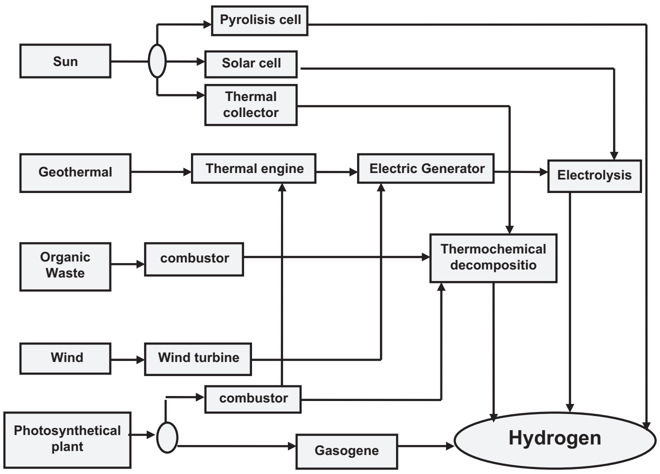


Fig. 2. Techniques of hydrogen production from renewable energies.

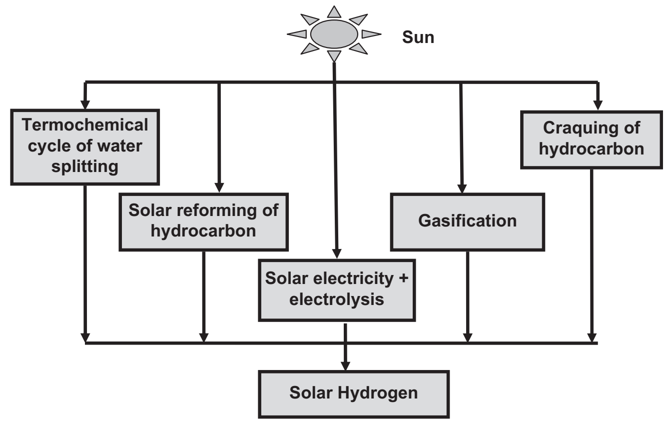


Fig. 3. An outline of the techniques of hydrogen production from solar energy.

production through fossils combustibles. Hydrogen provides the connecting point between renewable electricity production and transportation, stationary and portable energy needs. When the electricity from solar photovoltaics, wind, geothermal, ocean and hydro technologies is used to produce and store hydrogen, the renewable source becomes more valuable and can meet a variety of needs. In transportation applications, hydrogen provides a way to convert renewable resources to fuel for vehicles. Renewably produced hydrogen for transportation fuel is one of the most popular hydrogen economy goals, as it can be domestically produced and emissions-free. Recently, Koroneos and Dimitrios [12] have worked on the comparison of hydrogen production processes based on the exergy efficiency using various renewable energy sources. The Green methods for hydrogen production were also presented by Dincer [13] while Prospects and challenges of renewable hydrogen were discussed by Mazloomi and Gomes [14] and Abbasi [15]. In all the techniques involved in hydrogen production three things must be taken into consideration: The raw material, the energy necessary for the production and the process of production. For most of the processes, there exist relatively many important variants [16]. Fig. 2 below summarizes the different methods of hydrogen production from renewable energy sources such as wind, hydroelectricity and geothermal.

3. Hydrogen production from solar energy.

The techniques involved for the production of hydrogen from solar origin have attained a state of effectiveness and maturity thanks to the upcoming of new technological concepts and the creation of new solar thermodynamic stations [17]. These technologies enable the transformation of solar radiations into heat up to a temperature ranging between 200 °C and 2000 °C with a maximum efficiency of 70%. This primary heat will later be converted to an energy vector of hydrogen. Many different works have been realized for the promotion of solar energy as a primary source of energy production [18,19]. The techniques of hydrogen production through solar energy are summarized in Fig. 3.

3.1. Photochemical processes

Photochemical processes use solar light to produce the hydrolysis of water. Nowadays two procedures are known: the photobiological and the photoelectrochemical.

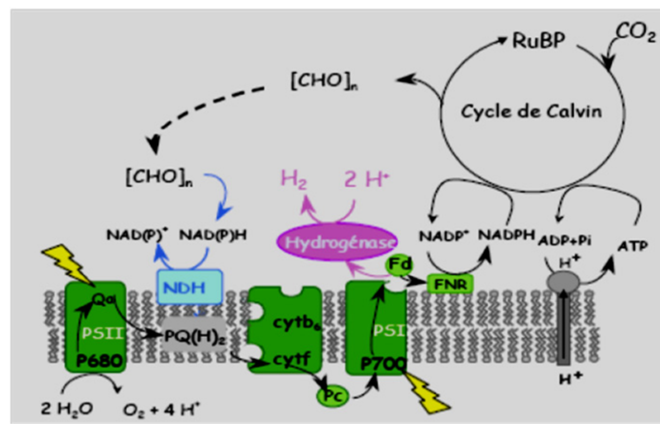


Fig. 4. Bio-production of hydrogen.

3.1.1. Bio-production of hydrogen from photosynthetic microorganisms

Photobiological processes are based on the capacity of some organisms, such as green algae, cyanobacteria, and photosynthetic bacteria, to act as biological catalysts in the production of hydrogen from water and different enzymes, such as hydrogenase and nitrogenase. Diversity in microbial physiology and metabolism means that there are a variety of different ways in which microorganisms can produce H_2, each one with seeming advantages, as well as problematic issues [20].

The H_2 metabolism of green algae was first discovered in the early 1940s by Hans Gaffron. He observed that green algae (under anaerobic conditions) can either use H_2 as an electron donor in the CO_2-fixation process or evolve H_2 in both dark and the light [21]. Although the physiological significance of H_2 metabolism in algae is still a matter of basic research, the process of photohydrogen production by green algae is of interest because it generates H_2 gas from the most abundant resources, light and water as shown on Fig. 4 [22–24]. Cystis pyrifera is the most convenient species because it has the highest growth rate of (50 t VS/ha yr) and can be harvested many times per year.

All microbial conversions can be carried out at ambient conditions, however lower rate of H_2 production and low yield are the main drawbacks. All processes are controlled by the hydrogen-producing enzymes, such as hydrogenase and nitrogenase. Hydrogenases exist in most of the photosynthetic microorganisms and they can be classified into two categories:

Table 2
Comparison of important biological H_2 production processes [25,26].

Process	General reaction	Advantages	Disadvantages
Direct biophotolysis	$2H_2O+high\rightarrow 2H_2+O_2$	Can produce H_2 directly from water and sunlight Solar conversion energy increased by ten folds as compared to trees, crops	Required high intensity of light. Simultaneous production of O_2 and H_2 Hydrogenase is highly sensitive to even moderately low concentration of O_2 Lower photochemical efficiency
Indirect biophotolysis	(a) $6H_2O+6CO_2+light\rightarrow C_6H_{12}O_6+6O_2$ (b) $C_6H_{12}O_6+2H_2O\rightarrow 4H_2+2CH_3COOH+2CO_2$ (c) $2CH_3COOH+4H_2O+light\rightarrow 8H_2+4CO_2$ Overall reaction $12H_2O+light\rightarrow 12H_2+6O_2$	Cyanobacteria can produce H_2 from water Has the ability to fix N_2 from atmosphere	Uptake hydrogenase enzymes are to be removed to stop degradation of H_2 About 30% O_2 present in gas mixture
Photofermentation	$CH_3COOH+2H_2O+light\rightarrow 4H_2+2CO_2$	A wide spectral light energy can be used by these bacteria Can use different organic wastes High substrate conversion efficiencies Degrade a wide range of substrates	Production rate of H_2 is slow O_2 has an inhibitory effect on nitrogenase Light conversion efficiency is very low, only 1–5% Pre-treatment may be needed due to either the toxic nature of the substrate (effluent), or its color/opaqueness. Large reactor surface areas requirement—Expensive equipment

(i) uptake hydrogenases and (ii) reversible hydrogenases. Uptake hydrogenases, such as NiFe hydrogenases and NiFeSe hydrogenases, act as important catalysts for hydrogen consumption. Reversible hydrogenases, as indicated by its name, have the ability to produce H_2 as well as consume hydrogen depending on the reaction condition. The major components of nitrogenase are MoFe protein and Fe protein. Nitrogenase has the ability to use magnesium adenosine triphosphate (MgATP) and electrons to reduce a variety of substrates (including protons). This chemical reaction yields hydrogen production by a nitrogenase-based system where ADP and Pi refer to adenosine diphosphate and inorganic phosphate, respectively

$$2e^-+2H^++4ATP\rightarrow H_2+4ADP+4Pi \quad (1)$$

The processes of biological H_2 production using solar energy can be broadly classified into following distinct approaches which includes: Direct biophotolysis, indirect biophotolysis and photofermentation.

The comparison of important biological H_2 production processes is summarized in Table 2 [25,26]. From an engineering perspective, they all potentially offer the advantages of lower cost catalysts (microbial cells) and less energy intensive reactor operation (mesophilic) than the present industrial process for making hydrogen.

However, several biological and engineering challenges must be overcome before this promising technology becomes a practical reality. Foremost, the cellular metabolism and basic biochemistry that support this process must be well understood and much fundamental research on the mechanism of H_2 production by S-deprivation remains to be done.

The diffusive nature of solar energy and the consequent low energy density places severe economic restrictions on potential light-driven processes for biological conversion of solar energy to hydrogen [20].

Other barriers to microbial based, large-scale production of H_2 include [27] [101] (a) inherent properties of the microbes that preclude continuity and efficiency of H_2 production; (b) underlying limitations of photosynthetic efficiency; and (c) limitations of the hydrogenase catalytic function.

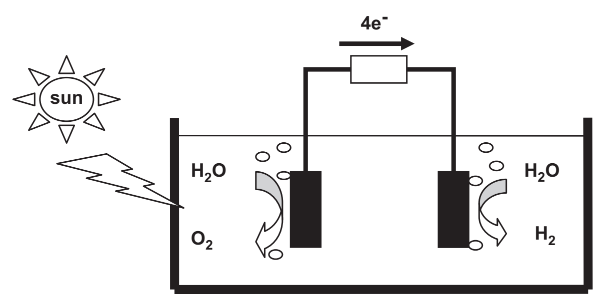


Fig. 5. Principle diagram for the photochemical decomposition of water.

3.1.2. Photo-electrolysis of water

Photo-electrolysis of water is the dissociation of a semiconducting photocatalyser by an electric current through lighting (Fig. 5). The photoelectrochemical cells (PEC) (photoactive electrodes) is submerged in an aqueous electrolyte or in water and is illuminated by solar light which can decompose water into hydrogen and oxygen. The thermodynamic cycles constitute a method of hydrogen production without the intervention of carbonized fossils by means of exhaustion and susceptible for the production of large amount of CO_2 responsible for the greenhouse effect. The decomposition process of water consists of realizing a thermal decomposition or a thermoelectrochemical decomposition of water with the supply (hence stocking) of solar energy thanks to a succession of reactions whose sum is equivalent to:

$$H_2O\rightarrow H+1/2O \ \Delta H=284 \text{ kJ/mole H} \quad (2)$$

The advancement of the direct decomposition is not significant (10%) for a temperature of 2800 K with $\Delta G=0$ at about 4700 K. taking into account the action of the intermediate stages enables the reduction of the reaction temperature. This answers the question on the decarbonization of the sources providing energy.

The cycles have been an active research objective during the decades 70–80, in particular with the aim of valorizing heat in nuclear reactors of type HTGR [28,29]. The research institutes for atomic energy (JAERI and GA) have developed works from the

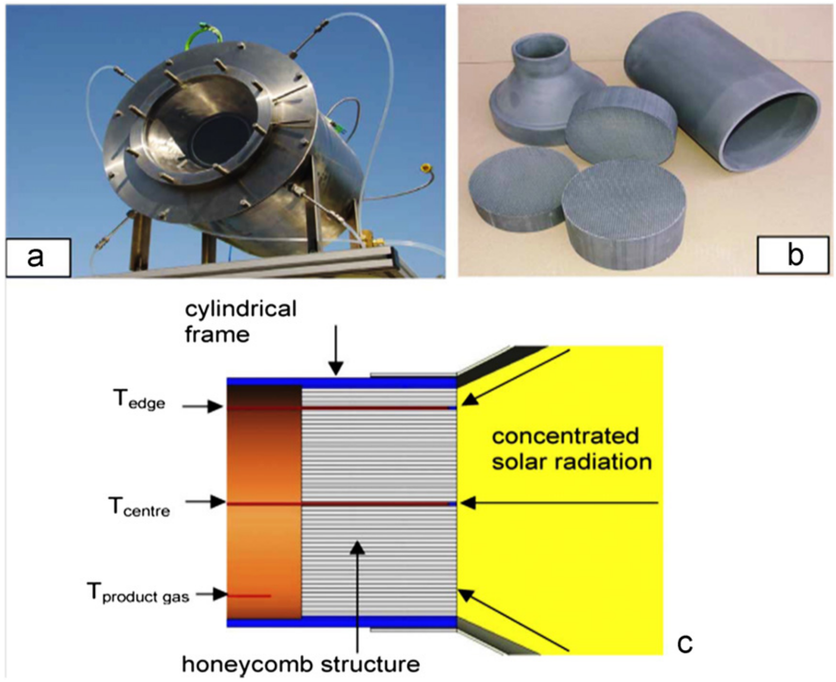


Fig. 6. Elements of the monolithic reactor for the dissociation of water [37].

basis of data obtained from cycles in order to select the most appropriate cycles and presenting superior level of temperature compatible with a heat source of nuclear origin (about 900 °C). The cycles generally retained are I-S and UT-3 [30]. The works of Research and Development on these cycles have been taken (in particular I-S) by the CEA recently in the framework of research on nuclear traces of the 4th generation.

The cycles with two or three stages and at temperatures greater than 900 °C constitute the most promising research channels for the solar path because it is very easy to be set up. The studied cycles in the setting of solar primary energy are principally cycles with basic oxides (2 stages) or the UT-3 and the I-S [31]. Concerning cycles with basic oxides like CdO/Cd and ZnO/Zn in the earlier 80 at IMP Odeillo [32], and most recently at Paul Sherrer Institute (PSI) in Switzerland [33] in collaboration with LSGC in Nancy [34] and the ferrite cycle [35]. These cycles involved a temperature of the order of 2000 °C using O_2 mixture (typical example: manganese–ferrite or nickel–ferrite cycle in Tokyo Institute of Technology permitting the step down of the cycle temperature [36].

The cycles with high temperature for instance sulphate or oxide present an important advantage of being very much easy but also necessitate an endothermic stage temperature of more than 850 °C. Meanwhile the taking into consideration criteria such as the non toxicity of the products and the simplicity of realization of the cycle are primordial for the success in terms of such production path; certainly more than the efficiency criterion within the framework of the use of a solar primary energy source. Agrafiotis et al. [37] had elaborated on a monolithic reactor for the solar dissociation of water with the aim of producing hydrogen. The different components of the system are represented in Fig. 6. Andrade et al. [38] have made proposition of a phenomenological modeling of photoelectrochemical cells with applications on non doped hematite electrodes for the production of hydrogen by thermal dissociation of water.

Photoelectrochemical processes are still under the stage of investigation. Their implementation is expected only in the long term.

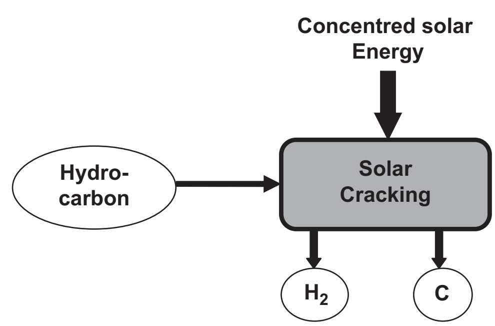


Fig. 7. Schematic of solar cracking process.

3.2. Thermochemical processes

Thermochemical methods for the production of hydrogen from solar energy includes: direct thermolysis of water, thermochemical cycles and cracking, reforming and gasification of hydrocarbons. These processes use concentrated solar radiation as high temperature heat source to carry out the endothermic reaction. Different devices are used to reach high solar concentration ratios: parabolic disks, tower systems and solar furnaces.

3.2.1. Solar cracking of hydrocarbon

The cracking of hydrocarbons consists in the realization of the co-synthesis of hydrogen and black carbon as shown in Fig. 7. The advantages of this method include [39]:

- The confinement and valorization of carbon contained in a natural gas in solid state;
- An economic emission of 14 kg CO_2/kg H_2 and energy from fossil origin of 277 MJ/kg of H_2. This is with respect to the other conventional methods of hydrogen production like steam reforming and charcoal (black carbon) [40].

The decomposition of methane for the production of hydrogen was proposed by Matovitch [41] in 1978. The developed reactor permitted the complete dissociation of CH_4 into fraction of seconds at a temperature of 2100 K. This method was later encouraged by Steinberg [42] and Muradov [43] in 1993. Thermodynamic studies of this reaction have elsewhere been proposed by Hirsch et al. [44] and Dahl et al. [45]. The endothermic reaction is presented below;

$$CH_4 \rightarrow C(s) + 2H_2 \ (\Delta H = 75 \text{ kJ mole}^{-1}) \ (190 \text{ kJ mole}^{-1} \text{ at } 2000 \text{ K}) \quad (3)$$

Thermodynamically, the decomposition of methane is theoretically complete within the neighborhood of 1300 K. Realistically, methane is very stable and the kinetic decomposition is not favorable whereas the properties of black carbon depend as well on the temperature of decomposition. These two factors have given preference to the reaction temperature to be much greater than 1500 K.

Two types of solar reactors have been put in place for the cracking of methane namely; direct [46–48] and indirect reactors [40–49]. Works have been engaged in Switzerland in PSI by Steinfeld et al. [35], then by Hirsch and Steinfeld [46], in USA by the National Renewable Energy Laboratory (NREL) [49], and in Israel by Kogan and Kogan [47,48] on the thermal and or catalytic decomposition of Hydrocarbons by solar channel, this is in order to decarbonize future combustibles. For example Dahl et al. [50] obtained a maximum conversion of 90% of methane at 2133 K from a mixture of Ar/CH_4 in a reactor of suspended particles («Aerosol Reactor»). At very low temperature Hirsch and Steinfeld [46] carried out experimental studies on the cracking of methane in a reactor directly irradiated with a power of 5 KW under a solar flux intensity of 2.8 MW/m^2.

The out flow of methane was loaded with Carbon particles which also served in the absorption of radiations and a reacting surface for the cracking process. In domains where the temperature ranges between 1510 and 1680 K, they arrived at the conversion of 44 to 66% of methane and measured a conversion of 67% in a solar reactor of vortex type. Study on the kinetic decomposition of methane in a solar reactor was realized by Rodat et al. [51]. This study was preceded by numerical simulation of the tubular solar reactor [52]. Many other authors [53–55] have equally landed on the modeling and simulation of heat transfer within suspended particles in an irradiated reactor. Rodat et al. [56] have experimented the production of hydrogen and black carbon in a prototype solar reactor with the experimental diagram (Fig. 8) described earlier [57].

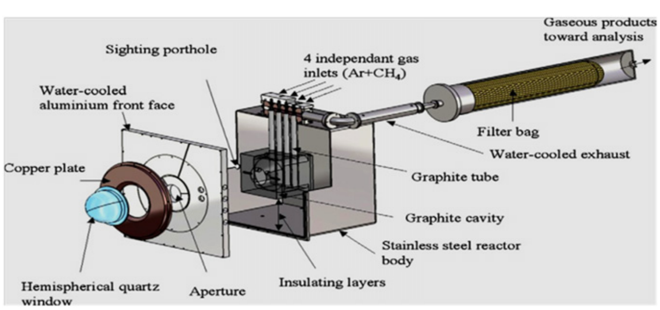


Fig. 8. Diagram of a solar reactor of capacity 10 kW and an Odeillo filter [50].

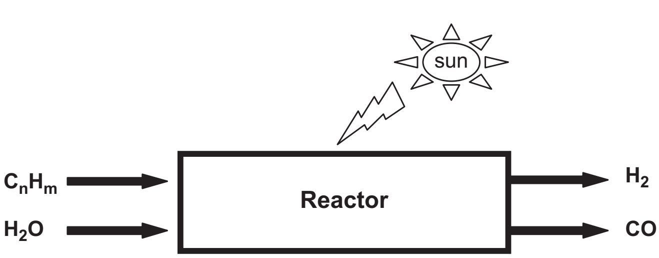


Fig. 9. Principle diagram for solar reformation.

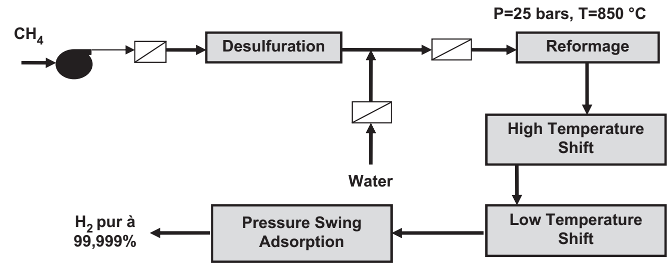


Fig. 10. Detailed principle diagram for steam reforming.

The cracking of methane as the afore works reveal is the most exploited channel for the production of hydrogen using the solar method in recent times. Unfortunately, this means of production consumes non renewable fossil resources and gives off polluting wastes.

3.2.2. The steam reforming of hydrocarbons

Steam reforming (Figs. 9 and 10) consists of the slow transformation of hydrocarbons into a synthesized gas by reacting them with water vapor in the presence of Nickel as catalyst [58,59]. This takes place at very high temperature range of 840–950 °C and at moderate pressure of the order of 20–30 bars. The pure hydrogen necessary for other use is put into action in the production chain which is relatively complex. In all cases of production, the composition within the steam reforming unit can be natural gas, methane, propane and even Napthaline. Natural gas essentially consists of methane which generally has to be desulphurized before being directed into the steam reforming unit. The two principal chemical reactions put in place are the production of synthesized gas and the conversion of CO:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \ (\Delta H = 206 \text{ kJ/mol}) \quad (4)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \ (\Delta H = -41 \text{ kJ/mol}) \quad (5)$$

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H \ (\Delta H = 165 \text{ kJ/mol}) \quad (6)$$

Reaction (4) is the steam reforming stage. It is an endothermic reaction and is characterized by an H_2/CO_2 stoechiometric relation of order 3. CO contained in the gas being dangerous is eliminated by the second reaction which permits restitution of hydrogen.

This second reaction corresponds to the conversion of CO into CO_2 (a process called water gas shift). It is slightly exothermic and more or less complete according to its realization in stage 1 or 2. These stages involve high and low temperature shifts reactions respectively gearing towards 400 and 200 °C. We thus obtained a gas essentially made up of H_2, CO_2 (16–20% in volume), H_2O, a little of CO and CH_4 [59,60]. Generally, the result of the two preceding reactions is endothermic.

The parasitic reactions for the decomposition of Hydrocarbons can equally take place and generally end with the formation of soot. These reactions can however be controlled by adjusting the rate of vapor injected into the reactor which permits the elimination of soot production. The following two stages consist of separating CO_2 and hydrogen and to eliminate the remaining traces of impurities principally methane and sub products of CO_2. Several works and projects have been realized on steam reforming throughout the world.

Marty [61] carried out a study on non catalytic steam reforming of Propane at high temperature in a solar reactor. Langnickel et al. [62] also carried out an experimental study on catalytic steam reforming of methane in a solar reactor that is directly irradiated and obtained a rate of hydrogen gas production oscillating between 45.8% and 53.1%. Rainer Tamme et al. [63] under the same conditions obtained a methane conversion rate of 87% with 49.3% of molar fraction of hydrogen in the output products from the reactor.

The CSIRO energy technology team [64] in Australia worked on the catalytic steam reforming of methane in a 46 KW capacity reactor of the same standard. Associated with a concentrator of type "dish engine" the reactor was capable of producing hydrogen for the supply of a fuel cell of type PEMFC of 10 kW. Buck et al. [65] simulated the catalytic reformation of methane with CO_2 in the same type of reactor. They did among others a simulation for the performances of the reactor according to the thermodynamic results (balanced) obtained and further predicted a methane conversion of 79.8% for an output gas temperature of 753 °C. The total thermal power absorbed was 322 KW for which 81% was for the chemical reaction and 14% for an increased in the sensitive enthalpy of the gas and a total gas flow of 0.102 kg/s. Levitan et al. [66] from Weismann Institute of Science equally studied experimentally the reformation of methane with CO_2 by the catalytic channel in a reactor that is indirectly irradiated. This reactor constitutes a cylindrical aluminum with interior diameter of 16 cm, 45 cm of length and partition thickness 1 cm. They characterized the reaction kinetics, the temperature level attained and they also led parametric survey. Menigault [67] used a porous medium (indirectly irradiated reactor) with its surface exposed to concentrated solar radiation for the heating of air. According to the nature of the porous surface used, he showed that higher temperatures can be attained.

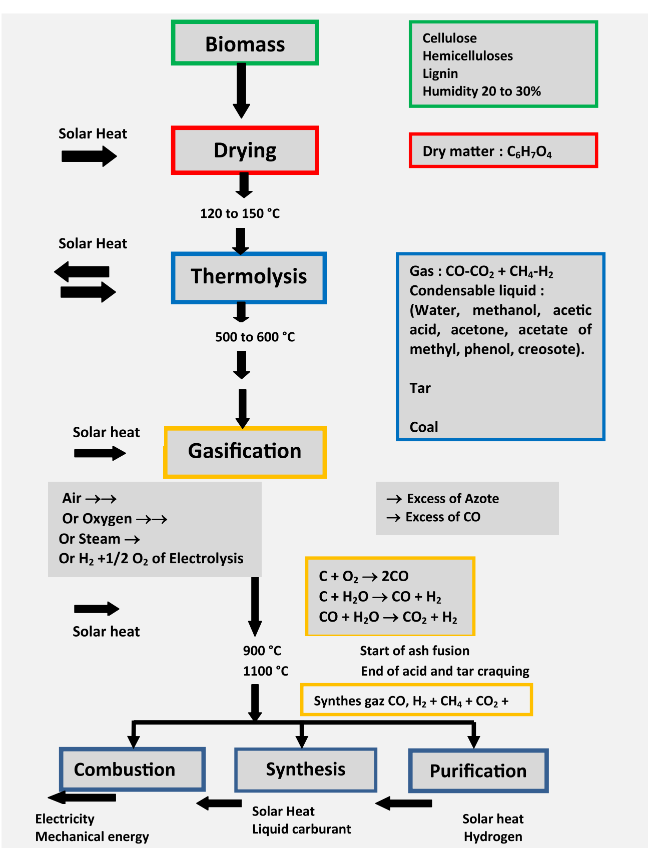


Fig. 11. Processes involved in the thermochemical transformation of biomass.

Just like the cracking process in the solar method, this technology consumes a lot of hydrocarbons and remains to be a debatable issue due to the exhaustive nature of fossils.

3.2.3. *Thermochemical transformation of biomass*

Biomass consists of all the plants growing on the earth surface. It is obtained from the photosynthesis of CO_2, H_2O and sunlight leading to the production of molecules, cellulose, Lignocellulose and lignin having the same composition as $C_6H_9O_4$. It can then be possible to regain stored energy in the combustible form [68,69] by more or less effective transformation on the energetic and economic platform. This is done through combustion, methanation, alcoholic fermentation and thermochemical transformations [70,71].

This method is particularly convenient for the valorization of lignocellulosic products such as wood or straw. This branch which leads to the gasification of organic substances [72], constitutes a successive chain of operations that necessitate the simultaneous transfer of physical quantities and the control of the proportion and times of reaction contacts at a given instant. Fig. 11 summarizes the different steps of operation. The processes of gasification currently represent a capacity of 430 million Nm^3 of the world's hydrogen daily production [73].

Generally, this can be translated through the following reaction:

$$C_6H_9O_4 + 2H_2O \rightarrow 6CO + 6{,}5H_2 \tag{7}$$

In case where we want to favor the production of hydrogen, supplementary hydrogen is obtained by the "gas shift" reaction as shown below:

$$6CO + 6H_2O \rightarrow 6CO_2 + 6H_2 \tag{8}$$

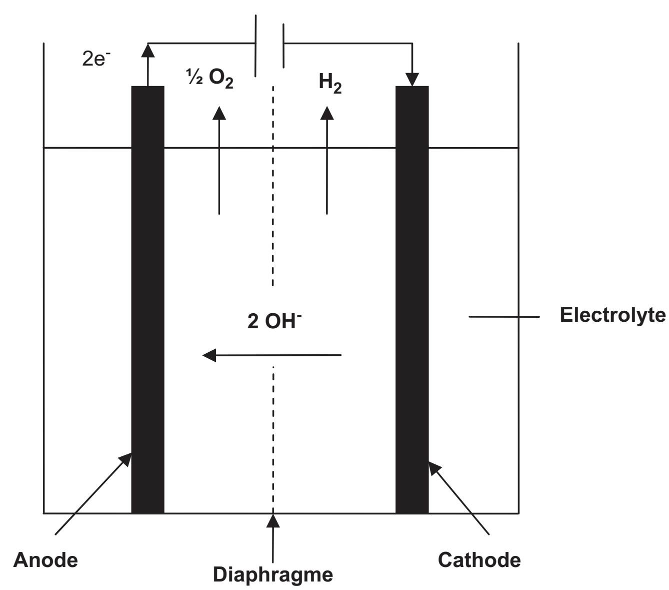


Fig. 12. Alkaline water electrolysis process.

Table 3
Characteristics of Värnamo, Sweden unit [64].

Power/heat generation	6 MW_e/9 MW_{th}
Fuel input (wood chips)	18 MW
Net electrical efficiency	32%
Total net efficiency	83%
Gasification pessure/temperature	18 bar/950 °C
Lower calorific value of product gas	5 MJ/Nm^3
Product gas steam pressure/temperature	40 bars/455 °C

Amongst the 12.5 molecules of hydrogen finally obtained, only 4.5 comes from biomass and 8 are brought by water which is only used as a reactive agent. We can also consider that the 6 molecules of CO_2 gas which is liberated does not contribute to the production of the greenhouse effect because they are the same molecules that the process of photosynthesis captures from the atmosphere for the growth of plants and which are recycled. Devi et al. [74], Maniatis [75] raised an inventory of fixtures of research link in the domain of gasification. The principal parameters to be considered are; the temperature of the process, pressure and type of gas chosen for gasification (air, vapor, oxygen, etc) (Fig. 12).

The first step of gasification is the pyrolysis of biomass. This stage has as a specific research objective the development of rapid pyrolysis [76–78] or torrefaction [79]. Another way of research is of course the optimization of the conception of the process [74] which will eventually allow improving the efficiency of the process.

Table 3 below presents the principal characteristics of unit of Värnamo (Sweden) which started in 1993. This unit is the heart of European project CHRISGAS, whose aim was production of fuel through the synthesis of hydrocarbon by gasification.

Biomass is potentially a reliable energy resource for hydrogen production. Biomass is renewable, abundant and easy to use. Over the life cycle, net CO_2 emission is nearly zero due to the photosynthesis of green plants. The thermochemical pyrolysis and gasification of hydrogen production methods are economically viable and will become competitive with the conventional natural gas reforming method. Biological dark fermentation is also a promising hydrogen production method for commercial use in the future. With further development of these technologies, biomass will play a role in the development of sustainable hydrogen economy.

3.3. Electrochemical processes

Apart from gas reformation, the electrolysis of water [80] is the most developed and useful method in industries for the production of hydrogen. Water electrolysis (Fig. 12) is an electrochemical process permitting the decomposition of water into its constituent elements of hydrogen and oxygen thanks to electrical energy [81], according to the two chemical reactions separately taking place at the anode and the cathode:

At the anode:

$$H_2O + \text{electricity} \rightarrow 2H^+ + (1/2)O_2 + 2e^- \quad (9)$$

At the cathode:

$$2H^+ + 2e^- \rightarrow H_2 \quad (10)$$

The general electrolysis reaction is

$$H_2O + \text{electricity} \rightarrow H_2 + (1/2)O_2 \quad (11)$$

The process of electrolysis can occur at both ambient temperature and at high temperature.

The electrodes are separated by an electrolytic conductor made up of ions which permit the easy transfer of ionic particles between the electrodes. In the course of the process, electrical energy provided to the system is then transformed into chemical energy in the form of hydrogen. The electrolysis of water is well known but not cost-effective on the economic base unlike the case where electricity was to come from a renewable source. The most important technologies in the electrolysis of water process are the alkaline electrolytes, the polymer membranes and the oxide electrolytes of ceramic, the electrolysis of steam [80,82,83] in which the efficiencies currently obtained from the electrolytic process are of order 65–85%. Among these technologies the electrolyzers PEM (Proton Exchange Membrane) are very practical for the production of high quality hydrogen. A review of the PEM technology electrolyzers has been done by Grigoriev et al. [84].

Agbli et al. [85] have developed a graphical model of the electrolyzer from macroscopic energetic representations. Other phenomenological models of electrically supplied electrolyzers by renewable energy particularly solar origin have been an objective of many works [86,87]. Vanhanen et al. [88], Galli and Stefanoni [89] succeeded in a small scale production of electrolytic hydrogen from photovoltaic solar energy. This prowess has equally been realized at an industrial scale by Szyska in [90,91] for fixed and mobile applications. At Forschungszentrum Jûlich in Germany, a technological unit of demonstration, PHOEBUS (Photovoltaik, Elektrolyseur,Brennstoffzelle Und Systemtechnik) has been installed for the production of electrolytic hydrogen from a voltaic fields of 43 kW [92].

Negrou et al. [93] have equally studied the development of hydrogen production by electrolysis in Algeria. They focused on the economic aspects and they also showed that the higher the quantity of hydrogen gas produced the lower is the cost of production of a kg of hydrogen. For an annual production higher than 4×10^6, the electrolytic hydrogen becomes more competitive than hydrogen produced by conventional sources (see Table 4). This result can be generalized to all other tropical country with strong solar potential and in which the electrolytic technology can be carried out for the production of hydrogen in high quantity.

High temperature electrolysis of steam (HTE) is expected to consume less electrical energy as compared to electrolysis at low

Table 4
Comparison on hydrogen production cost: case study Algeria [84].

Production capacity (kg/year)	10^6	2×10^6	4×10^6	8×10^6
Conventional source (€/kg H_2)	3.41	3.35	3.31	3.28
Solar tower (€/kg H_2)	11.45	7.54	4.75	3.25

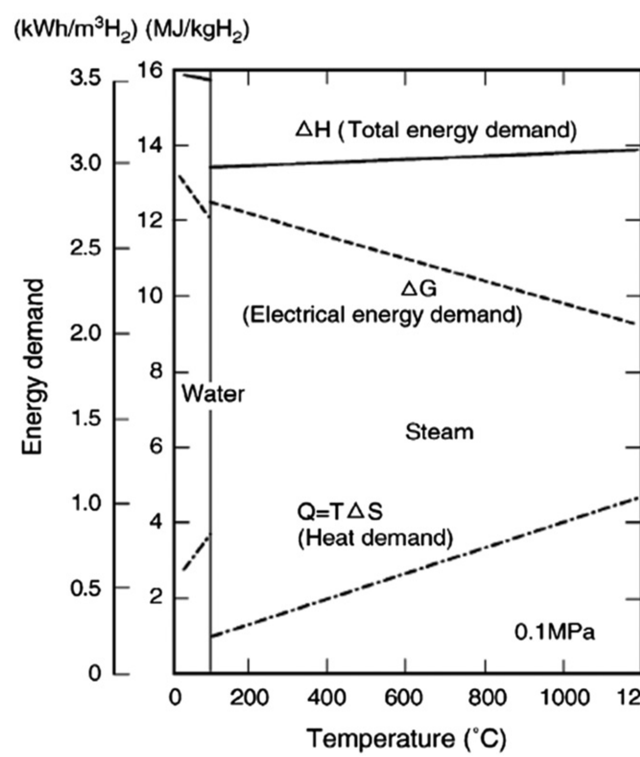


Fig. 13. Energy demand for water and steam electrolysis.

temperature (Fig. 13) as a consequence of the more favorable thermodynamic and electrochemical kinetic conditions for the reaction [94].

Thermodynamic conditions are more favorable in the sense that the molar Gibbs energy of the reaction (ΔG) drops from $\sim$1.23 eV (237 kJ mol^{-1}) at ambient temperature to $\sim$0.95 eV at 900 °C (183 kJ mol^{-1}), while the molar enthalpy of the reaction (ΔH) remains essentially unchanged ($\Delta H \sim$1.3 eV or 249 kJ mol^{-1} at 900 °C) [95]. A significant part of the energy required for an ideal (loss free) HTE can thus be provided by heat. Solid oxide steam electrolysis (SOSE), is a promising technology if used in conjunction with renewable energy [96,97].

The main commercial advantages of hydrogen production by electrolysis are its scalability and the emission-free production of hydrogen (when produced via renewable energy). There are challenges to setting up mainstream electrolyzer use for hydrogen production, primarily high capital costs and the cost of electricity. For example, PV electricity today costs approximately $ 30/kw-hr, perhaps ten times what is needed to make electrolysis cost competitive, and the cost of electrolyzers themselves must be significantly reduced to enable large-scale implementation.

4. Comparison and outlook

4.1. Exergy efficiency of the different processes

The comparison of the various processes associated with the solar hydrogen production can be done through exergy efficiency which gives an idea of the amount and the quality of useful energy that can be completely utilized in useful work and the sustainable index which tells how sustainable a system is in actual practice. The exergy efficiency and corresponding sustainability index for the different process of solar hydrogen production are shown in Figs. 14 and 15. The sustainability index for the electrolysis process of Ni et al. [98] is 2.7 respectively and for Balta et al. [99] it varies from a minimum of 4.76 and a maximum of 7.14 with respect to the minimum (473 K) and maximum (1173 K) operating temperatures. The reason for Balta et al. electrolysis possess higher sustainability index is that the unit has higher exergy efficiency as they have used high temperature electrolysis. The corresponding sustainability index for solar decomposition of Natural gas, for solar steam reforming of Natural gas and for solar steam gasification of coal are 1.47, 1.85 and 1.85, respectively [100]. It should be noted here that despite of the higher exergy efficiency of the electrolyzer, charge regulator and inverter units, the system exergy efficiency is still low. It is mainly because of the low PV exergy efficiency. There is a need to improve the PV array efficiency in order to have better sustainability index and hence better sustainability.

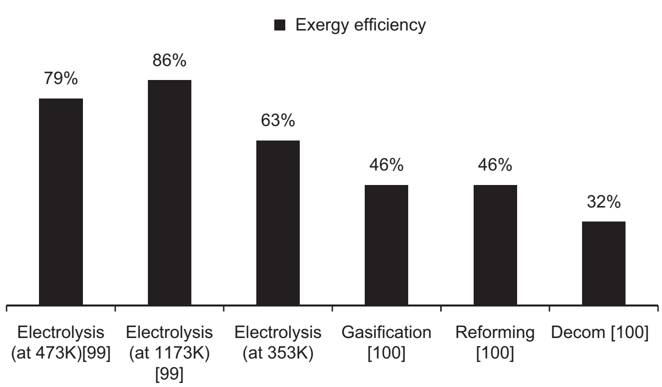


Fig. 14. Exergy efficiency of the different processes of solar hydrogen production.

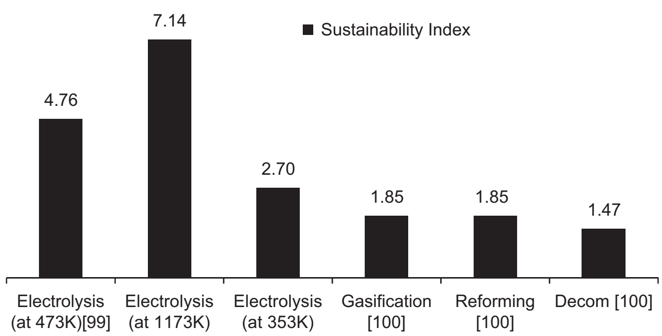


Fig. 15. Sustainability index of the different processes of solar hydrogen production.

Table 5
Projected costs (long term) of hydrogen production (€/t of H_2) [89].

Current process designs and small scale pilot plants	**Cost (€/ton of H_2)**
Solar hybrid sulphur cycle	1900
Solar sulphur–iodine cycle	2000
Solar metal/metal oxide cycle	3500
Solar high temperature electrolysis	4667
Solar methane cracking	1767
Solar methane steam reforming	1633
Other future renewable options	**Cost (€/ton of H_2)**
Biomass gasification	1067
Alkaline electrolysis using photovoltaic power	6667
Alkaline electrolysis using solar thermal power	2667
Alkaline electrolysis using wind power	2333

4.2. Economic comparison

Table 5 shows the projected costs (in the long term) of hydrogen production (€/t of H_2) using the commercial available technologies presented in this paper. Costs values of hydrogen production from other future renewable options and actual large-scale commercial plants consuming fossil fuels are also presented in Table 5 for comparison purposes.

Steam methane reforming is nowadays the more competitive available technology for the production of hydrogen from an economical point of view. Table 4 shows how the conventional SMR has production costs of 1200 €/t of hydrogen. With carbon capture and storage technologies (CCS), SMR become more expensive.

However the development and implementation of CCS systems is a pre-requirement for the hydrogen scenario in order to meet the ambitious goals of the world environmental policy.

Among related technologies for the hydrogen production through solar energy, only solar methane steam reforming could become cost competitive. Nevertheless, the costs of this technology depend on natural gas availability and prices. Same consideration corresponds to solar methane cracking. It is expected that their high hydrogen production cost will noticeably decrease as prices of methane and carbon decreases.

Water electrolysis is considered a promising hydrogen production method although the hydrogen cost by electrolysis would be very high as compared to the other mature technologies such as steam methane reforming. But taking into account the environmental benefits help and the effective utilization of by-product oxygen of electrolysis for a medical or industrial use the process efficiency and cost can be improved.

Biomass gasification can also be competitive despite the fact that biomass is mainly used in the production of biofuels, for cooking and other residential use (in poor countries). Therefore, a limited potential of this type of hydrogen production technology is expected.

Within this scenario, an opportunity for those regions with high solar potential appears. The tropical regions of the world in general, the Middle East, the large majority of African countries, some European and American region have the possibility to become world powers in solar hydrogen generation. A proper policy could help not only the production of hydrogen for internal consumption, but also, in the long term, the export of intercontinental energy to other hydrogen markets.

5. Conclusion

The various methods for utilizing solar energy for hydrogen production were examined and both their advantages and disadvantages are compared in terms of exergy efficiency, sustainability factor and economic efficiency. If perhaps the cracking and steam reforming of hydrocarbons have additional attributes, yet they remain limited by their non renewable fossil energy character and their environmental impacts. Electrolysis of water for tropical countries with strong solar radiations potential is an interesting option which assumes much development with high temperature electrolyzers commercialization.

The solar-to-electricity conversion efficiency is the main limitation in the improvement of the overall hydrogen production efficiency. By comparison, solar powered electrolysis, photoelectrochemical and photochemical technologies can be more advantageous for hydrogen fueling stations because fewer processes are needed, external power sources can be avoided, and extra hydrogen distribution systems can be avoided as well.

High temperature processes need further materials development which focuses on high temperature membranes and heat exchangers for solar thermal processes. Therefore the world's solar hydrogen utilization systems consist mainly of photovoltaic hydrogen systems for transportation and stationary applications. Ecofriendly hydrogen production via solar is very important to save environment as it does not emit any greenhouse gases during operation. At present it is a challenging task for researchers and scientists as the exergy efficiency of the PV array is low and hence, the overall exergy efficiency of a solar hydrogen system.

Many of the renewables have sitting, social, or environmental concerns which also must be overcome. However, all these barriers are being addressed aggressively by government and industry, and it is worth considering whether the benefits warrant greater investment today.

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